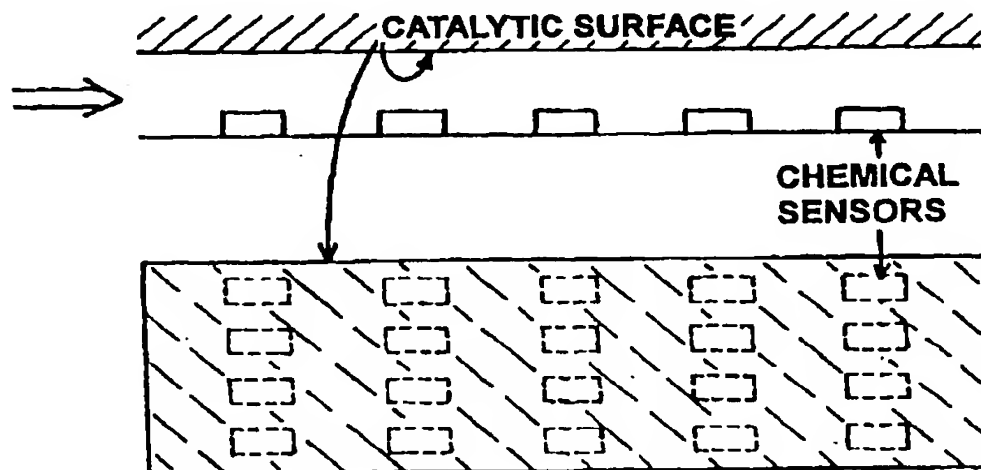




## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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<b>(21) International Application Number:</b> PCT/SE96/00908 <b>(22) International Filing Date:</b> 4 July 1996 (04.07.96) <b>(30) Priority Data:</b> 9502688-6                      25 July 1995 (25.07.95)                      SE <b>(71) Applicant (for all designated States except US):</b> NORDIC SENSOR TECHNOLOGIES AB [SE/SE]; Teknikringen 6, S-583 30 Linköping (SE). <b>(72) Inventors; and</b> <b>(75) Inventors/Applicants (for US only):</b> LUNDSTRÖM, Inge- mar [SE/SE]; Färgaregatan 10, S-582 52 Linköping (SE). SUNDGREN, Hans [SE/SE]; Gunnorp Bäckgård, S-590 50 Vikingstad (SE). <b>(74) Agent:</b> BERGLUND, Erik; Berglunds Patentbyrå AB, As- pebråten, S-590 54 Sturefors (SE).		<b>(81) Designated States:</b> AL, AM, AT, AU, AZ, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IS, JP, KE, KG, KP, KR, KZ, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, US, UZ, VN, ARIPO patent (KE, LS, MW, SD, SZ, UG), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).  Published With international search report.

(54) Title: METHOD AND DEVICE FOR THE EXPANSION OF SENSOR SELECTIVITY



## (57) Abstract

Electronic odour detecting device (electronic nose) provided with a number of sensors. The gas that is to be subjected to the detection is brought to pass a number of similar or different sensors distributed on a surface. Between the sensors or actually extending between and past the sensors is a catalyst. The catalyst may be arranged on an opposing wall in a detection cell or in the same surface as the sensors. Constituents of the gas that react with the catalyst result in a different signal pattern for the sensors depending on their location in relation to the catalyst. Since different substances in the gas will react with different rates in the presence of the catalyst the sensed pattern will change along the catalytic surface. This makes it possible to evaluate a gas mixture with great precision and with a more limited number of sensors in comparison to prior art. In order to enhance the selectivity of the different sensors the catalytic surface may also be held at different temperatures at different areas of the measurement cell. In the same cell also patterned catalytic surfaces may be arranged.

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### Method and device for the expansion of sensor selectivity

Gas sensors sensitive to different molecules are known. Such sensors are normally not totally selective but have different selectivity patterns. It is known to combine such sensors in order to analyze gas mixtures and odours. By comparing the obtained response patterns with previous test results using a computer remarkable precise results can be obtained regarding the identification, classification and also quantification of gas mixtures and odours.

The combination of a number of sensors and a pattern recognition routine is known as an "electronic nose" [Sensors and Sensory Systems for an Electronic Nose, (J. W. Gardner and P. N. Bartlett, eds.) Nato ASI Series E, vol. 212, Kluwer Academic Publishers, 1992]. The electronic noses have numerous applications within process and food industry, medical diagnosis, control of combustion processes and monitoring of the environment to mention a few.

Modern computers have improved the possibility to use pattern recognition methods to identify the response pattern from different sensors to different odours. Many different sensors are available and in many cases a number of set ups may have to be tested and even combined to provide a correct analysis in the end. This is in particular since it is not only desirable to know which molecules that are present in the mixture but it is also in many cases important to know their actual concentrations. This constitutes a problem since the sensors thus may have to detect very small quantities of material or very large quantities of the same. Too sensitive sensors will not be able to indicate great amounts correctly and too insensitive sensors will not give indication at all of lower concentrations. In order to obtain a versatile electronic nose sensors with different selectivities and sensitivities are necessary. Furthermore, the choice of the sensors will depend on the particular application. As a result of the above difficulties the electronic noses of today are not very versatile and may in some instances require very large number of sensors and data power making them rather expensive and slow.

Another problem encountered is the lack of selectivity, that is, many sensors react on many gases almost identically, making it difficult to tell them apart and necessitating additional sensors etc.

The objective of the present invention is to provide a method by which the analyzing power of chemical sensor arrays can be expanded and a more exact as well as a more versatile device for the monitoring of gas mixtures and odours. In accordance with the invention this is achieved by using a new sensing principle based on a geometrical distribution of sensors and catalysts. This arrangement gives a number of possibilities for the enhancement and control of the signal pattern from a sensor array for a given gas mixture.

In this new sensing method according to the invention the gas or gas mixture that is to be analyzed is brought to pass a catalyst simultaneously with detection by sensors. Many of the gas components that are desirable to monitor react in one way or the other in the presence of a catalyst. This means that the gas passing over the catalyst will change in its proportions of different molecules. This in turn can be detected since sensors placed along the catalyst will give different readings. Since different molecules react in different ways in the presence of a specific catalyst a recognizable pattern specific to the mixture will be obtained in the gas flow direction along the catalyst.

The sensors can be arranged in the catalyst itself or in fact catalysts and sensors may constitute top and bottom in a gas analyzing cell, provided that the height is not too large, since the change in the composition due to chemical reactions at the catalyst must influence also the sensors in order to provide the recognizable pattern. Such a measuring cell can be provided with a varying set up of catalysts or catalytic surfaces and indeed several different catalytic materials can be used in for instance strips in the cell and also different sensors can be used. A set up change can however be obtained also in other interesting ways. To start with the thickness of the layers of catalytic materials can vary along the flow path. Also the temperature of the sensors and/or the catalytic materials may vary along the flow path or crosswise of the flow path in order to provide suitable recognizable patterns. The size of the catalytic areas and the temperature of these influence the concentration/alteration of the gas components and the temperature of the sensors influence the sensitivity of the sensors. Suitable catalytic materials are platinum, palladium, iridium as well as other organic or inorganic materials, including semiconducting materials.

The presence of a catalyst may at the same time change gas components that are not measurable with the used sensors into components that can be measured or sensed by the sensors and at the same time other components that can be sensed can be changed into

components that are not sensed by the used sensors.

One of the major advantages of the invention is the above mentioned possibility to construct in a simple way sensor cells that can easily be switched between a number of different selectivity patterns. It gives the possibility to use a modular system comprising one or two dimensional sensor matrices or arrays and a catalytic surface or even an array or matrix of catalysts comprising areas of different catalytic materials that can be combined to give a device with a great number of different selectivity patterns. Top and bottom in an analyzing cell can be combined to provide the desired selectivity and sensitivity, which efficiently reduce the number of sensor arrays that has to be kept in store. Since the catalytic part (for instance top) need no or only few (temperature control) electrical connections substitution can be carried out in simple mechanical ways.

Further advantages and features of the invention are apparent from the following description of preferred embodiments described in connection with enclosed drawings where in fig 1 and 2 is shown what happens when a gas passes a catalytic surface, fig 3 a and b show a gas sensing cell and example of possible sensor signals, fig 4 top and bottom of a cell with catalyst and sensor patterns, fig 5 catalyst and sensors on a common substrate, fig 6 a and c the signal response from a device as shown in fig 6 b.

The invention is thus based on the fact that catalytic materials (not only metals but also semiconductors, insulators, organic materials, zeolites etc.) efficiently consume molecules and make new molecules by reactions on the surface of the material as it is schematically shown in fig 1. This means that if a stream of gas is passing over a catalytic surface the concentrations of gas components A and B are reduced while the concentrations of the reaction products AB, X and Y increase (fig 2). This effect is in the invention used to analyze a gas mixture since the different parts of the mixture are used up/react with different rates along the surface. This is in fig 3 depicted with two components U, W that when reacting in the presence of the catalytic surface give rise to the products S and P, respectively (only U and W are shown in fig 3). By arranging the catalytic surface for instance in the top of the flow cell and place chemical sensors along the bottom of the flow cell, sensitive to U, W, P and/or S the reaction pattern can be measured and with this the composition of the gas mixture can be analyzed. This possibility is shown schematically in fig 3. More complicated patterns are obtained if also S and P can be detected.

The flow cell in the device in fig 3 should be so thin that the consumption/making of molecules at the catalytic surface is observed also at the other wall of the flow cell (that with the chemical sensors). The distance is ruled by for instance flow rates and the reactivity of the catalytic surface and the available pressure differences between in- and outlet of the flow cell. This distance can however vary within wide limits, for practical reasons however between 0,001 and 10 mm. The length of the flow cell is determined partly by the reactivity of the catalytic surface and of the number of chemical sensors that are placed along the channel (and the type of these). Lengths between 1-100 mm are therefore probable. The width of the flow cell is essentially decided by the sensor technology that is used and of the total gas flow that is to be accommodated. The width is however not the critical parameter and can therefore be varied within wide limits. In fig 3 a is shown four sensor rows where each row can consist of sensors with the same or different selectivity patterns in relation to different types of gases or molecules.

If desirable the cell may also comprise walls separating the flow over different areas of sensors, coinciding with the strips of catalytic materials or more or less crosswise of these.

One of the unique features of the invention is the increased combination possibilities that are achieved when the device according to fig 3 is used. The catalytic activity depends on choice of catalytic material and its temperature. Surfaces with "patterns" of consumption and production of molecules can therefore be fabricated. Also many chemical sensors (based for instance on semiconducting metal oxides, field effect transistors etc.) have a temperature dependent sensitivity and selectivity. By varying the temperature along the sensor matrices and/or the catalytic surface therefore a number of different response patterns can be obtained with given catalytic surfaces and sensor matrices.

Fig 3 b shows an example where a temperature gradient ( $T_1 < T_2$ ) exist along the sensor matrix and the catalytic surface and where the consumption of U and W on the catalytic surface is increased with the temperature and where the sensitivity of the sensors for U and W also increase with the temperature. In this case maxima of the response to U and W along the sensor matrix are obtained. The position of the maxima are in general different for U and W. An interesting observation is that the sensors in the example in fig 3 b may be entirely unselective for U and W. The catalytic consumption of the molecules will however provide selectivity.

It is apparent that the device in fig 3 can be given considerable analytic ability by for instance making bands of catalytic materials with different selectivity/activity for different classes of molecules and make areas or rows of chemical sensors with different selectivity patterns for different classes of molecules. Fig 4 schematically illustrates these possibilities. The sensors can for instance be field effect transistors with a thin layer of platinum, a thick layer of palladium and a thin layer of iridium. Mixtures of sensor technologies can also be used, for instance two rows with field effect transistors and one with semiconducting metal oxide (so called Taguchi-sensors). The areas of sensors and the catalytic bands need not to be overlapping but may be separated. Fig 4 shows that we can also consider having different temperature gradients along the sensor areas and the catalytic surface. Further options regarding the temperature is to have the gradients not along the areas or bands but in a optional angle in relation to these.

The invention constitutes a great improvement over the prior art since it allows the use of sensors that can not in themselves find any difference between different molecules, but together with the arrangement of a catalyst can. To start with molecules that do not react or do react in the presence of the catalyst will be told apart immediately. However even molecules that do react at the same catalytic surface will be possible to differentiate between since the maximum of the response (signal) will be found at different locations in the cell, this since they will react with different rates in the cell.

The invention also constitutes a great step forward as regards sensor elements for electronic noses since both the catalytic surfaces and the sensor areas can be standardized and need only to be combined to provide the final selectivity pattern. In an electronic nose it is required that the sensors provide signals, the patterns of which vary with the mixture of the blend of gases (odours). The suggested device is here very useful. The device can be built in different ways. The sensor areas can be arranged in any angle in relation to the catalytic areas, which increase the number of possible selectivity patterns further. Sensors with different selectivity need not to be arranged in rows but can be arranged in any two dimensional pattern. This also goes for the catalytic surface. Sensor and/or catalytic areas can be made on the same substrate or on separate substrates.

Catalytic metals such as palladium, iridium, platinum, ruthenium and alloys of them convert organic molecules with a rate that is ruled by the choice of metal and temperature. Sensors

also exist for the majority of organic molecules, for instance field effect transistors with gates made of catalytic metals or sensors based on semiconducting metal oxides ( $\text{SnO}_2$ ,  $\text{TiO}_2$ ). Such sensors can be made small and with ease in rows. There is thus also the possibility to make a number of sensor rows on each substrate. This can be used either to increase the number of selectivity patterns (different sensors in two or more rows) or to obtain a device with redundancy (sensors of the same kind in more than one row) and therefor a better accuracy and long term stability.

Fig 5 shows another interesting possibility, namely the fabrication of the sensor and the catalytic areas on the same substrate. The above mentioned dimensioning rules are still applicable with the addition that in this case the size of the catalytic areas and the distance between these and the sensors should be small in order to couple the reactions of the catalytic materials efficiently to the sensors. The size of this measure (b) depends on the reactivity of the catalytic materials and the flow rate of the gas mixture that is analyzed. Typically this measure should be less than a few millimeters. The number of possible combinations and types of patterns is again very large. The advantage with the arrangement according to fig 5 is that the device not necessarily has to be used in a flow cell. The use of the device as shown in fig 5 in a flow cell with a lid with catalytic material, that is in a configuration similar to that in fig 3, is of course also a possibility that further increases the number of selectivity patterns. The device according to fig 3 has the advantage that by simply changing the lid with catalytic pattern new selectivity patterns can be obtained with the same sensor matrices as before (or vice versa).

It should be pointed out that also other arrangements than the above described are possible. There is nothing that prevent catalytic materials, for instance in the shape of a tube or a helix (in a cylindrical flow cell) to surround the sensor array.

In fig 6 a simple example is depicted showing the method of the invention. Assume that we have two substances a and b in the gas mixture which are "consumed" on the catalytic surface with a temperature gradient. This will result in a reduction of the number of molecules along the surface of the catalyst depending on the properties of the molecules. The different properties of the molecules will provide different concentration profiles along the catalytic surface. A number of sensors is provided along the bottom surface and the signals from these are ruled by the concentrations of the molecules and the temperature of the



sensors. This means that in the signal pattern obtained from the different sensors shown in fig 6 c, and corresponding to the curves shown in fig 6 a as calculated, molecules will provide different maxima which can be used to recognize the different molecules present, making, the otherwise unselective sensors selective. Of course more than two components may be told apart in this way.

The used discrete sensors may be arranged on a catalyst or surrounded by one or indeed several different catalysts in a suitable pattern, for instance strips. At the same time one or several catalyst may be arranged in a suitable pattern opposite to the sensors, for instance in a lid or roof of a sensor cell. This pattern may include strips of different catalysts that may be the same as those surrounding the discrete sensors or different from these or in an other order. The pattern may also contain strips angled in another direction than the sensors or catalyst strips on the same substrate as the sensors.

The invented way of gaining in selectivity may be used in combination with known sensors and may in fact be used to improve already fabricated devices.

The invention enables simple adaption to new odors by changing the catalytic surface, the sensor array, temperature and the temperature gradients along the catalytic surface and sensor array.

The detection in accordance with the invention need not to be static during sensing but may instead be varied, preferably periodically during the sensing procedure. This is very easily achieved by rotating the catalyst top part in a sensing cell. Also the temperature or temperatures of the catalysts and sensors may vary.

The invention provides an increase in available selectivity patterns and the computer may use its own judgement to pick out the best set up for detection of the various components.

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### Claims

1. Method for gas detection, characterized in that at detection is carried out with at least two sensors arranged in the vicinity of a catalyst in such a way that a flow of the gas mixture after passing the first sensor may react in the presence of the catalyst, then to be sensed by the second sensor.
2. Method according to claim 1, characterized in that the catalyst is arranged continuously between or past the sensors.
3. Method according to claim 1 or 2, characterized in that several sensors are arranged in the flow direction of the gas.
4. Method according to claim 1, 2 or 3, characterized in that several different catalysts are arranged along a row or area of sensors.
5. Method according to any of the claims 1 to 4, characterized in that the temperature of the catalyst is given a gradient crosswise or along the flow.
6. Method according to any of the claims 1 - 5, characterized in that the sensor have different temperatures.
7. Method according to any of the claims 1 - 6, characterized in that the flow direction or temperature of the sensors or catalysts vary during sensing.
8. Device for gas detection according to claim 1, characterized in that it includes at least two sensors and a catalyst arranged in such way that one of the sensors analyze or sense the mixture at the first location in the flow of the gas and the second sensor analyze the gas after its passing of the catalyst or while it is passing the catalyst.
9. Device according to claim 8, characterized in that the catalyst is in the shape of a band or area over which the gas stream flows.
10. Device according to claim 8 or 9, characterized in that several sensors are arranged in the direction of the flow in one or several rows along the catalytic material.
11. Device according to claims 8 to 10, characterized in that sensors and catalysts are arranged facing each other.
12. Device according to claims 8 to 11, characterized in that the catalyst is constituted by areas of different catalytic materials.
13. Device according to any of the claims 8 to 12, characterized in that the catalytic material has different thickness or is present in varying quantities in different areas.
14. Device according to any of the claims 8 to 13, characterized in that the catalyst

constitutes top or bottom in a measurement cell and the sensor array constitutes bottom or top in the same cell.

15. Device according to claim 14, characterized in that top and/or bottom are easily exchangeable.

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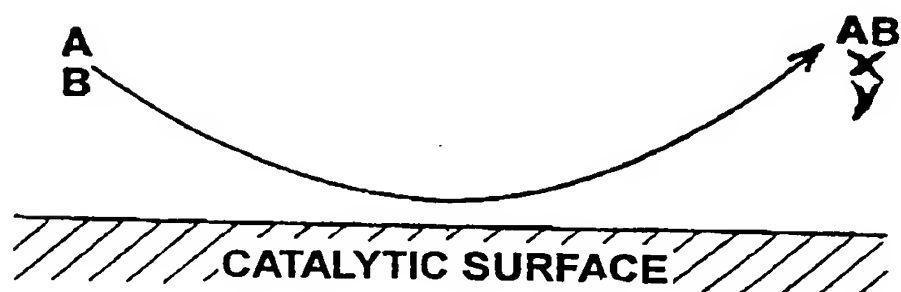


FIG. 1

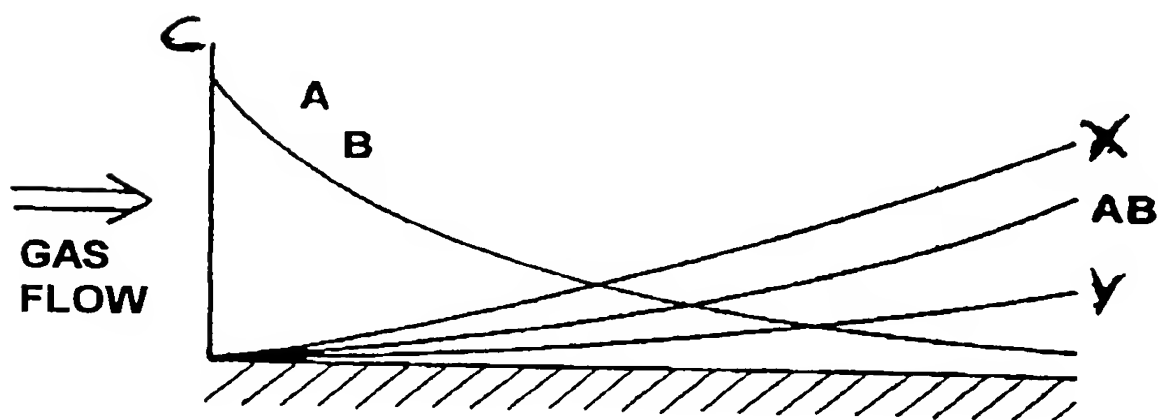
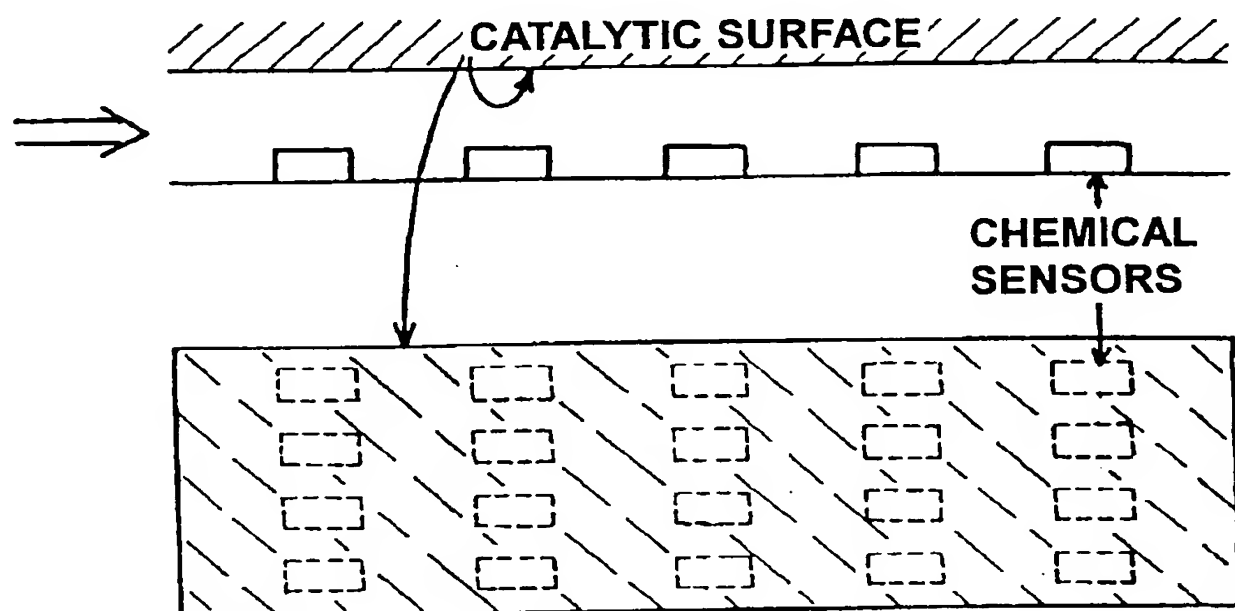
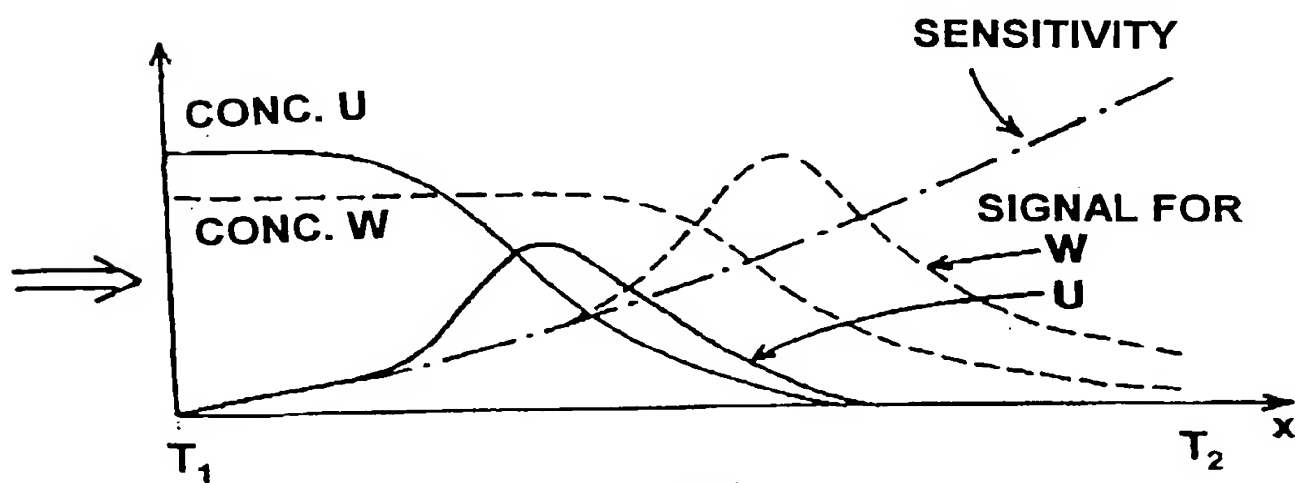


FIG. 2

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(a)



(b)

FIG. 3

3/4

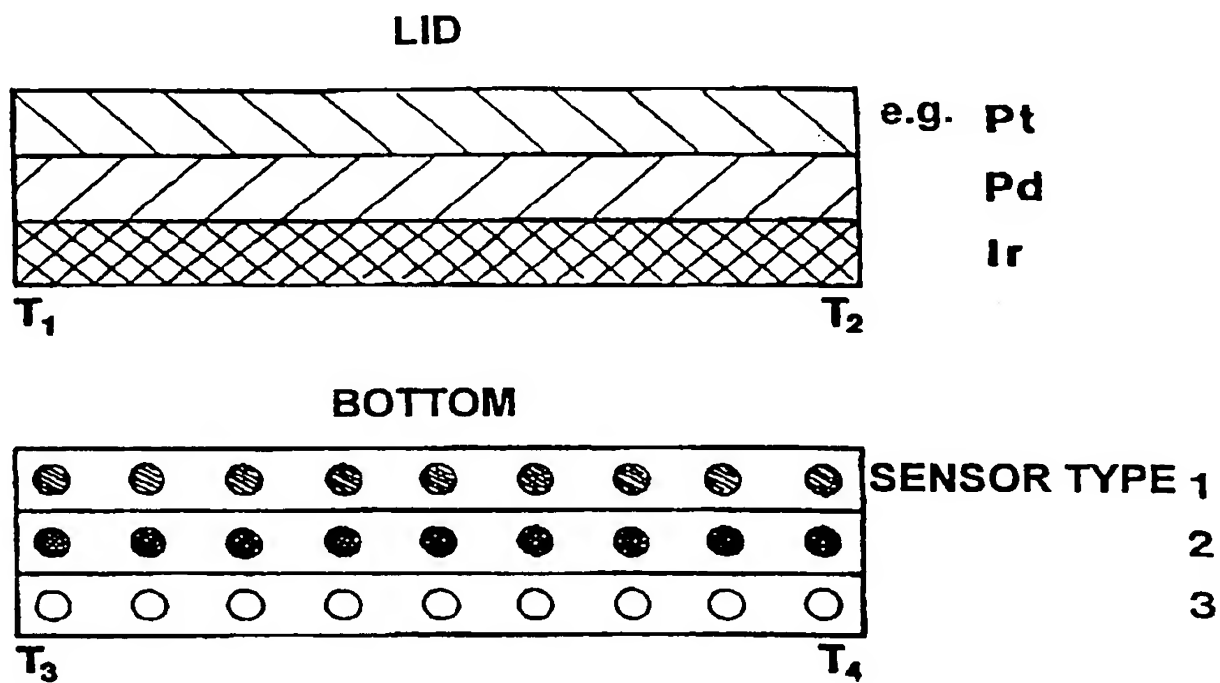


FIG. 4

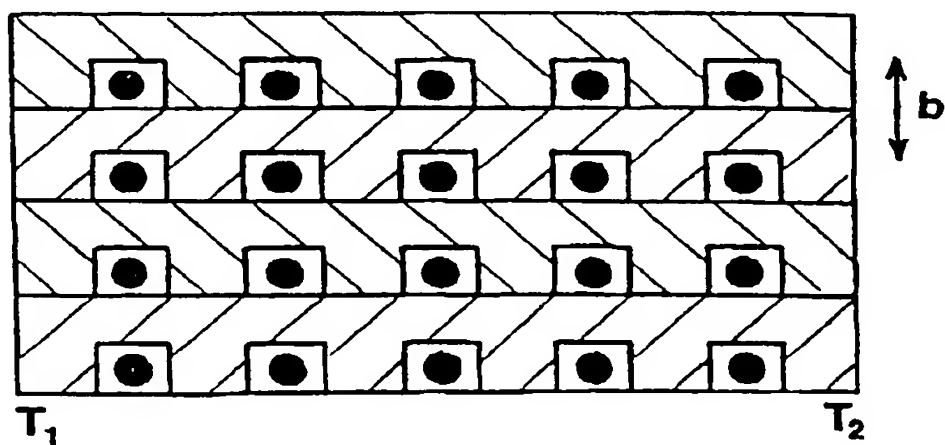


FIG 5

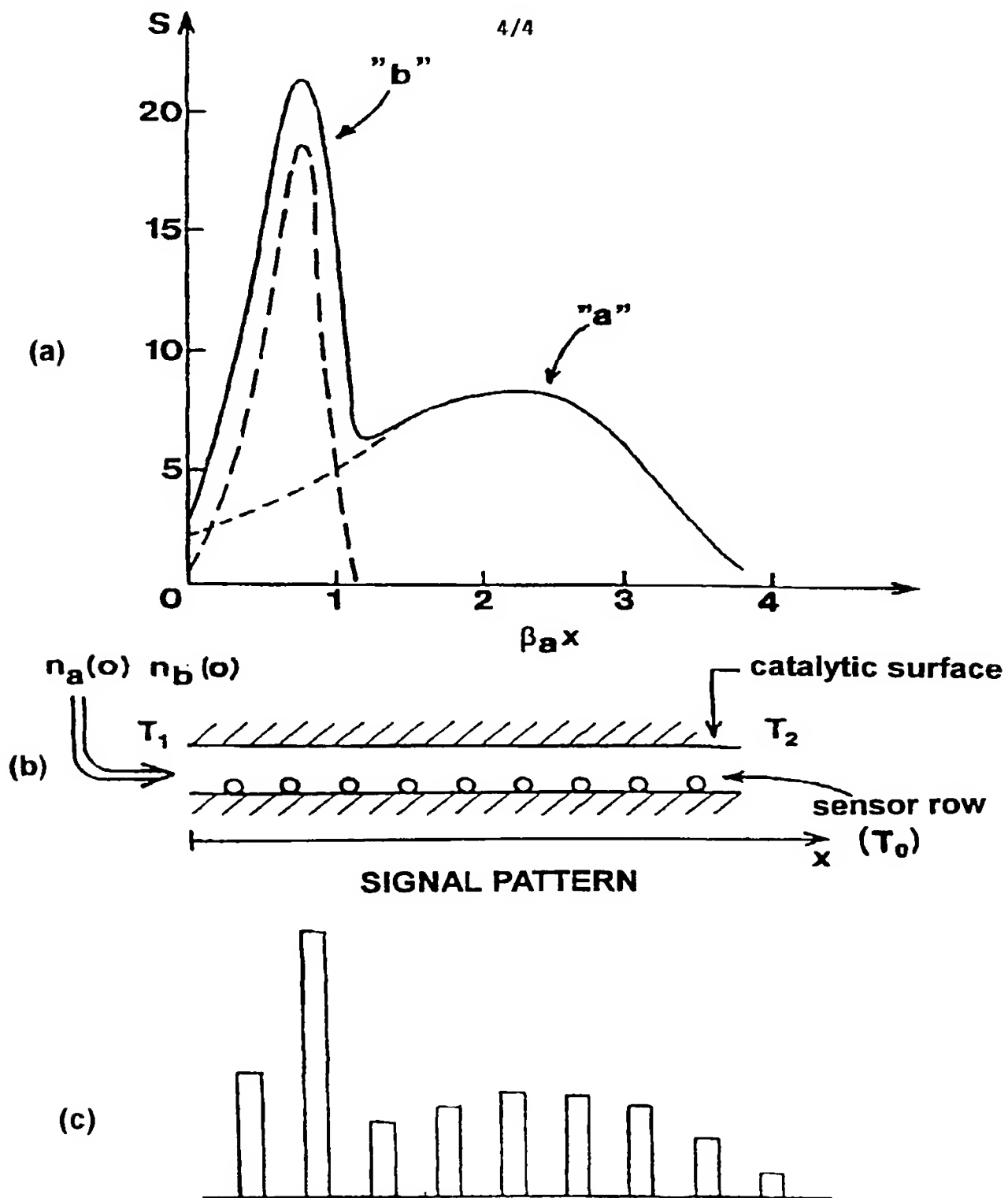


FIG. 6

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/SE 96/00908

## A. CLASSIFICATION OF SUBJECT MATTER

IPC6: G01N 27/16, G01N 31/10

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC6: G01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

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WPI, INSPEC

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	CH 665908 A5 (CERBERUS AG), 15 June 1988 (15.06.88), page 4, column 1, line 16 - column 2, line 51, figures 6-9	1-10,12
A	--	11,13-15
X	EP 0305963 A1 (DRÄGERWERK AKTIENGESELLSCHAFT), 8 March 1989 (08.03.89), column 3, line 54 - column 4, line 53, figure 1, abstract	1-3,5-11
A	--	4,12-15

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## INTERNATIONAL SEARCH REPORT

International application No.

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## C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4885929 A (KASAHARA ET AL), 12 December 1989 (12.12.89), column 7, line 4 - line 23, figure 9	1,8
A	--	2-7,9-15
A	SENSORS AND ACTUATORS, Volume 18-19, 1994, P.-M. Schweizer-Berberich et al, "Characterisation of food freshness with sensor arrays" page 282 - page 290 -----	1-15

# INTERNATIONAL SEARCH REPORT

Information on patent family members

01/10/96

International application No.

PCT/SE 96/00908

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
CH-A5- 665908	15/06/88	EP-A- 0141089 JP-A- 60061651 US-A- 4584867	15/05/85 09/04/85 29/04/86
EP-A1- 0305963	08/03/89	DE-A, C- 3729286 DE-A- 3868789 JP-A- 1072046 US-A- 4992384	16/03/89 09/04/92 16/03/89 12/02/91
US-A- 4885929	12/12/89	CA-A- 1297948 DE-D, T- 3887617 EP-A, B- 0311439 JP-A- 1096546 JP-B- 6095082	24/03/92 15/09/94 12/04/89 14/04/89 24/11/94